

VII. Crude Oil RefiningJanuary 3, 1944Item #267

## Crude Oil Refining at Iutzkendorf in 1943

A one page yield summary of oil distillation and treating operations (copy attached). Combined with Item #254 (flow sheet dated November 14, 1938), it gives a picture of conventional steps such as atmospheric-vacuum primary distillation of crude, propane deasphalting and dewaxing of heavy distillates and residues, phenol solvent refining of the motor and aircraft oils, along with the recovery of gasoline and kerosine.

Crude charged in 1943 114,151 tons

<u>Primary distillation</u>	<u>tons</u>	<u>%</u>
Naphtha	9,421	8.3
Kerosine	22,896	20.1
Spindle oil I	19,508	17.1
II	11,365	9.9
III	7,300	6.4
Hy oil distillates	11,537	10.1
Residuum	31,520	27.6
Loss	604	.5
	<u>114,151</u>	<u>100.0</u>

Produced

Naphthas	9,421	
Kerosine	20,000	
Spindle oils	3,524	acid treated
Total luboils (aviat., motor, etc.)	12,887	(dewaxed, phenol ref'd. & clay contacted)
Asphaltic residues	13,431	
Wax products	5,449	
Phenol extracts	10,785	
Heavy flux residues	31,520	

The throughput of intermediate departments was as follows:

Propane deasphalting of vacuum residues

Yield Hy oil	18,709 tons
" asphalt residue	13,431 "
Loss	163 "
Charged in 1943	<u>32,303 "</u>

Propane dewaxing of oil distillates

Yield of oils	21,004 tons
" " wax products	5,449 "
Loss	159 "
Charged in 1943	<u>26,612 "</u>

Phenol refining of oil distillates

Yield of raffinates	18,596 tons
" " extracts	10,785 "
Loss	158 "
Charged in 1943	<u>29,539 "</u>

Acid treating of oil distillates

Yield of treated oils	3,524 tons
Loss	107 "
Charged in 1943	<u>3,631 "</u>

Clay contacting of oils

Yield of finished oils	12,887 tons
Loss	68 "
Charged in 1943	<u>12,955 "</u>

No date (copy attached)

Item #266

A flow diagram of a phenol refining plant prepared by Friedrich Uhde, Engineers, Dortmund. Contains heat balance data.

August 23, 1938

Item #255

A part (second sheet) of a flow diagram of propene deasphalting and dewaxing prepared by F. Uhde, Engineers, Dortmund, with material balance data.

Lutzendorf, November 14, 1938

Item #254

A general flow sheet (copy attached) showing the inter-relation of the following 3 plants at Lutzendorf.

- (1) Fischer-Tropsch plant for making gasoline from coal gas,
- (2) Crude oil distillation for luboils, kerosine, naphtha and residues,
- (3) Hydrogenation plant for making gasoline from heavy residues.

The 75,000 ton/yr Fischer Tropsch plant starts with brown coal, produces the CO/H<sub>2</sub> gas, desulfurizes it in two stages and converts it, in contact ovens, into hydrocarbons. Liquid condensate from the gas is fractionated into heavy naphtha, kerosine and gas oil cuts. Charcoal absorption gasoline from the top gas is combined with the cracked naphtha to produce gasoline. The heavier distillates are cracked to produce additional quantities of gas, naphtha and residuum. The latter is sent to the hydrogenation unit.

The 100,000 ton/yr crude oil plant is described under #267. Its primary purpose is the production of lubricating oils, while naphtha and kerosine are subordinate products. The plant appears to be modern as it is equipped with an atmospheric-vacuum pipestill, has propane deasphalting and dewaxing facilities, and finishes the cylinder, aero and motor oils by phenol solvent refining and clay contacting. It is significant that all asphaltic residues and phenol extracts are sent to the hydrogenation plant.

The 50,000 ton/yr hydroplant is oversized to take care not only of pressure still tar from the cracking of heavier Fischer-Tropsch products, of phenol extracts and asphalts from luboil refining, but also of coal tar received from outside. The charging stocks are mixed and fed to a distillation unit. The overhead, called, "medium oil" is hydrogenated in reactors with a fixed catalyst bed. The residuum, called "heavy oil", is hydrogenated using catalyst slurry. Hydrogasoline is separated from the reaction products in a fractionating tower, and the heavier cuts are recycled to the reactors. Although not shown on the flow sheet, the hydroplant produces also Diesel and Marine fuel oils according to indications in production reports elsewhere in the file.

Selected Abstracts

Item #247

VIII. Miscellaneous

May 27, 1943

Excerpts from Report on the Lebedev Method of Manufacture of Synthetic Rubber

Up to 1941, Russia had 5 Buna Works. 30,000 tons/year capacity each, in production.

Plant	SK1	in	Yaroslav	-	Lebedev	process
	SK2	"	Voronesh	"	"	"
	SK3	"	Yefremov	"	"	"
	SK4	"	Kazan	"	"	"
	SK5	"	(?)			
	SK6	"	Kursk		Some other process in	construction

Method of Manufacture at SK3

Grain alcohol is delivered as a raw 84-86% product and mixed with recycle alcohol from the process. This combined feed has the following composition:

Ethylalcohol	80%	Hydrocarbons	.1-.2%
Acetaldehyde	2-3.5%	Water	Balance
Ether	.5-1.0%		

This alcohol is vaporized in pipestill and heated to 110°C @ 1.2-1.3 atm, at a rate of 270-300 m<sup>3</sup> per day. From 18 to 20 catalytic furnaces are in operation on the average. There are 30 furnaces at Yefremov, each containing 16 rectangular steel retorts .1 x 1 x 5 m in size and holding the catalyst (a mixture of Mg and Al silicates and carbonates). Alcohol vapors from the pipestill are preheated to 390-410°C before entering the catalyst bed in which the temperature is held at 385-390°C. After 12 hours of operation the catalyst contains 2-3% carbon and must be regenerated. This is done by blowing an air-steam mixture at 600°C until outgoing gas contains no CO<sub>2</sub>.

The reaction is endothermic requiring 500-600 cal/kg of alcohol. Water content of over 30% in the alcohol lowers the yield of butadiene, while up to 20% of aldehyde has no such effect. However, aldehyde decomposes easier and cokes up the catalyst.

Product of Reaction (Outgoing Vapors)

30-32% Butadiene\* (highest observed 35%)  
 2.5-3.0% Acetaldehyde  
 .5% Ether  
 1.0-1.5% Higher alcohols  
 .5% Ethylene  
 10.0-20.0% Hydrogen, CH<sub>4</sub>, CO (fixed gases)  
 App. 40% Alcohol

\* Includes 5-10% of butylene

The outgoing vapors are passed through water coolers and brine coolers. At minus 2°-minus 3°C, the noncondensed gas contains 42% butadiene. It is compressed to 6 atm. and scrubbed first with 86% alcohol and then with water. At this stage the bulk of alcohol, water, aldehydes and fixed gases is removed. Further processing is fractionation at 27-32°C under 2.7 atm. pressure and the final step is drying in potash towers. Composition of purified butadiene:

92-93% butadiene  
 .02% alcohol  
 .03% water  
 trace aldehyde  
 Balance butylene

The polymerization of the butadiene is conducted in vapor phase, and the butylene content serves to control the rate of the reaction of polymerization.

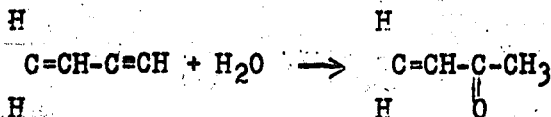
There are 58 vertical steel autoclaves  $\phi$  1.35 m, H 2 m., for polymerization in vapor phase. Metallic sodium in paste form is held on 18-20 horizontal shelves. The reaction continues for several days. There are also 8 horizontal autoclaves  $\phi$  1.5 m., length 10 m., into which the containers with paste can be introduced more conveniently. A part of butadiene is polymerized in liquid phase in 120 vertical autoclaves each equipped with 60-65 suspended bars coated with sodium. The latter, in turn, is protected with paraffin wax from the action of air.

"Conference with Dr. Stadler, Dr. Sandhees, and Mr. Buchert on November 30, 1942"

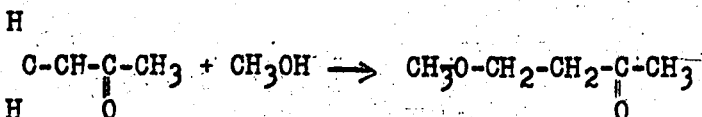
Item #119

Subject: DIMOL

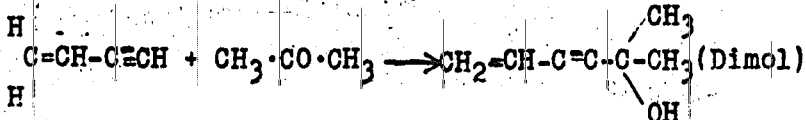
Dr. Stadler stated that at present 130 kg/day of vinyl acetylene can be made. The installation for the preparation of 450 kg per day is in construction and is to be completed very soon. Dr. Daniel discussed mixed polymerization (co-polymerization). In further discussion, the possibility of preparing vinyl methyl ketone from vinyl acetylene was presented.



By the use of methanol therewith, the ether is obtained:



The preparation of Dimol from vinyl acetylene and acetone



The reaction is carried out with potassium hydroxide and it is essential that the potassium hydroxide be very finely ground. The Dimol is formed from its alkali salt. Dimol boils at a temperature of 146°C at atmospheric pressure with decomposition, so it should be distilled in vacuo. The alkali salt is converted, by addition to water, into Dimol, which is not water soluble, and concentrated

potassium hydroxide solution. The reaction of vinyl acetylene with acetone is carried out in the proportion of 1.6:1.

Memo

At a conference with Dr. Eckell on 12/1/42, at which others were Dr. Daniel and Dipl. Ing. Valentin, Dr. Eckell was informed about our Dimol plans as follows:

The supply of acetylene for the preparation of vinylacetylene could be obtained from methane cracking. The cost of construction for the preparation of two tons per day of vinylacetylene is about 370,000 RM (\$92,000 at 25¢ RM). The structural steel requirement is not known. The acetone supply similarly was expected from the Sachsse plant in the amount of two tons per day. The investment for the preparation of three tons per day of Dimol from vinylacetylene and acetone is about 280,000 RM (\$70,000 at 25¢/RM) and requires 240 tons of steel machinery, 30 tons of structural steel and 1.2 tons of copper.

Co-polymerization with butadiene takes place in the ratio: three parts Dimol to seven parts butadiene. According to Dr. Daniel, the ratio is 22 parts Dimol to 78 parts butadiene.

Oppau, September 11, 1941

Item #120

This item shows a plant diagram for the Dimol production of three tons per day.

The raw materials used were given as:

7480 kg vinylacetylene  
2147 kg potassium hydroxide  
1740 kg acetone

The yield of reaction product was 3000 kg of Dimol.  
(Some parts of the photostat are not legible.)